

Investigating the Interdiffusion of MgO and CaO

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An atomistic model was used to calculate the mutual solubility of MgO and CaO compounds. Interdiffusion of MgO and CaO was found to be more energetically favourable than maintaining separation. Density functional theory calculations, as implemented by CASTEP, supported these findings and were able to find optimal crystal structures of specified sizes. Further to this, the pairwise potential calculations suggested the encapsulation of Ca atoms was the most energetically favourable configuration for a non-crystalline structure.

I. Introduction

The interdiffusion of metal oxides (MOs) is currently poorly understood, despite the well-understood applications of metal-oxide interfaces for protective coatings and catalysis. It is necessary to understand the interactions of MO layers, as their useful properties (such as being thermally insulating and semiconductive) are applied to improve technologies such as lithium ion batteries. [3]

In this investigation, the interdiffusion of two metal oxides with a face-centred cubic (FCC) structures, MgO and CaO, was modelled and the internal energy of their mixed structures measured.

II. Method

The internal energy of the MO compounds were found through density functional theory (DFT) calculations with CASTEP. [1] A program was written to compare the energy of different ratios of metals in a crystal structure, relative to the separated compounds. The script was extended to test the lowest-energy configuration of the metal ions in the unit cell, according to DFT.

As well as this, an additional program was written to compare the ground state energy of finite clusters for varying ratios of metal oxides. Initially, a lattice was generated with two domains consisting of MgO and CaO, forming a defined interface. The ground state energies were found using a Metropolis-Hastings algorithm [2], where two different random cations were swapped and the lowest energy configuration was accepted. The lattice energies were calculated using a pairwise potential, which consisted of the sum of the Lennard-Jones and Coulombic potentials, shown in equation 1:

$$V_{ij}(r) = 4\epsilon_{ij} \left[\left(\frac{r_{ij}}{\sigma_{ij}} \right)^{-12} - \left(\frac{r_{ij}}{\sigma_{ij}} \right)^{-6} \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where r_{ij} is interatomic distance, q_i , q_j Hirshfeld charges and σ_{ij} , ϵ_{ij} are parameters of, respectively, the potential and atom-type at sites i and j . A script was developed to run simulations for a given set of parameters, produce figures and .xyz files which can be used to visualise the structure in Jmol.

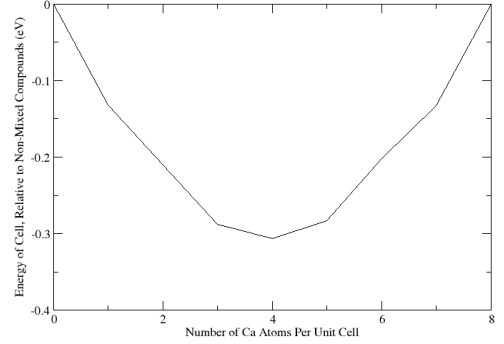


FIG. 1: Graph showing the DFT-calculated energy of a 16-atom MgO and CaO unit cell relative to non-mixed MgO and CaO crystal structures.

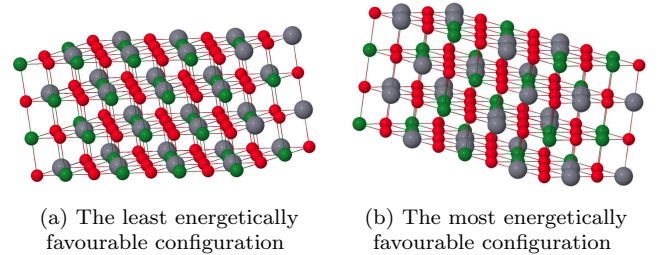


FIG. 2: 16-atom unit cell structures of $\text{Mg}_4\text{Ca}_4\text{O}_8$. Oxygen - red; magnesium - green; calcium - grey.

III. Results

The DFT method suggest that MgO and CaO do mix, with an even split of the metals in the unit cell being most energetically favourable. The relative energy of the two oxides, plotted against their ratio in the unit cell, can be seen in figure 1.

An energy difference was found between certain arrangements of metal ions in a 16-atom unit cell, as calculated with CASTEP. Crystal structures with Mg and Ca atoms alternating down the plane, as can be seen in figure 2a, were found to be in a higher energy state than those with the ions paired up - see figure 2b.

The atomistic model predicts that MgO and CaO mix, with equal amounts of each being most energetically

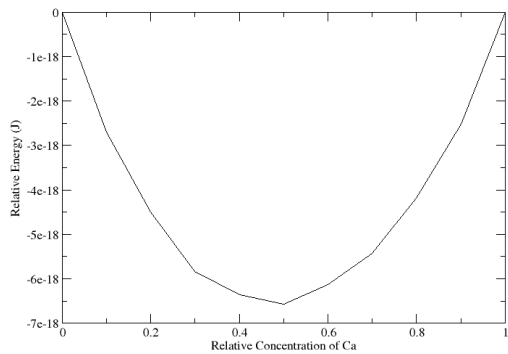


FIG. 3: Graph showing the ground state energy relative to non-mixed MgO and CaO structures for varying Ca concentrations, produced by the Metropolis-Hastings model, for a 729-atom cluster at 300K.

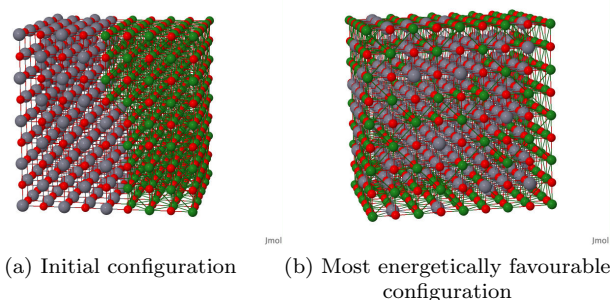


FIG. 4: 729-atom cluster, 50/50 ratio and at 300k. Oxygen - red; magnesium - green; calcium - grey.

favourable, forming a convex hull over varying concentrations of Ca. This is shown in figure 4a. Figure 4 and figure 5 show the initial configuration of the system, followed by the ground state configuration. The Ca structure within the crystals are shown in fig 6.

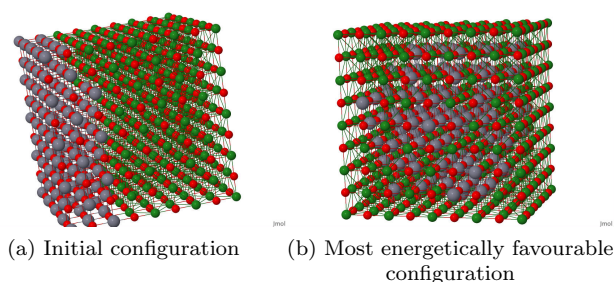


FIG. 5: 729-atom cluster, 30/70 Ca:Mg ratio and at 300k. Oxygen - red; magnesium - green; calcium - grey.

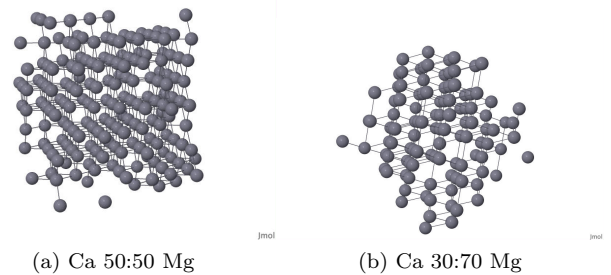


FIG. 6: Calcium atom positions within the most energetically favourable state for a 729-atom system at 300K.

IV. Discussion

The results strongly indicate that it is beneficial for magnesium and calcium oxides to mix in a 1:1 ratio when combined in a face-centred lattice structure. This is shown by figures 1 and 3, where the two alternative approaches correspond with each other; MgO and CaO separated into separate compounds are in a higher energy state than when the metal ions are mixed. These two models show this to be the case for a large range of temperatures - from ground state energy to 300K.

When the most favourable of the atomic configurations are investigated, however, grouping of the metal ions is observed. The DFT model, limited to small unit sizes, had Mg and Ca in separate pairs. When modelling a non-crystalline structure with the atomistic model, the calcium ions were observed to cluster in the centre of the structure, with magnesium ions lying on the outside. This may be due to the form of the potential. MgO is less stable compared with CaO, with reference to the potential used. Thus, a structure in which Ca clusters in the middle will place Ca ions in a more energetically favourable state, whilst simultaneously placing Mg ions as far from one another as possible, reducing their potential energy.

V. Conclusion

Simulations of MgO and CaO crystal structures show that interdiffusion of these two compounds should be expected when they are combined. However, a homogeneous mixture of the two should not be presumed.

- 570, 2005.
- [2] M. Eckert, E. Neyts, and A. Bogaerts. *CrystEngComm*, 11:1597–1608, 2009.
- [3] Y. Wang, Y.-F. Zhang, H.-R. Liu, S.-J. Yu, and Q.-Z. Qin. *Electrochimica Acta*, 48(28):4253–4259, 2003.